



NO_x removal by rhodium catalysts supported on carbon nanotubes: Evidence for the stoichiometric reduction of NO₂ and NO by the carbon support

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ABSTRACT

The catalytic removal of NO and NO₂ over rhodium particles supported on carbon nanotubes (Rh/CNT) was studied in the absence and presence of oxygen. It was found that the stoichiometric oxidation of the carbon support by adsorbed oxygen deriving from the rhodium-catalyzed scission of NO is crucial to achieve steady-state conversion of NO_x. The proposed reaction pathway is verified by complete nitrogen and oxygen balances. In the absence of excess oxygen, Rh/CNT catalysts exhibit high activities in the catalytic reduction of NO and NO₂ with the carbon support acting as the reducing agent. Oxidative pretreatment of the CNT support enhances the catalytic activity. The lifetime of the catalysts is limited by the stoichiometric oxidation of the support material. The structural degradation during the time on stream is evidenced by transmission electron microscopy.

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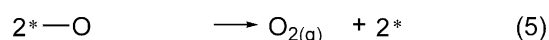
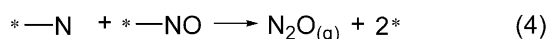
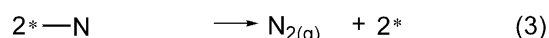
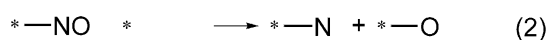
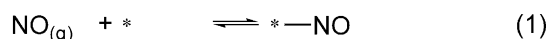
1. Introduction

Nitrogen oxides (NO_x) originating from industrial and automotive emissions are major air pollutants. They contribute to the depletion of stratospheric ozone, the generation of tropospheric ozone and the formation of acid rain. The catalytic removal of NO_x under lean-burn conditions is one of the most important targets in environmental catalysis research. Various NO_x control technologies such as the direct decomposition, NO_x storage-reduction (NSR) and selective catalytic reduction (SCR) using different reducing agents (ammonia, diesel soot [1], carbon monoxide [2] or hydrocarbons [3]) are constantly advanced. The direct decomposition of NO_x is the most eligible approach as no reducing agent is needed and no harmful side products are formed.

NO is a thermodynamically instable molecule with an enthalpy of formation of 90.2 kJ/mol. Accordingly, its decomposition into the elements is thermodynamically favoured at temperatures below 1000 °C, yet kinetically hindered due to a high activation barrier of 335 kJ/mol, making the use of catalysts indispensable.

Catalysts that have been reported to be active in the decomposition of NO_x can be divided into three major groups:

zeolites, metal oxides and noble metals [4]. Supported rhodium catalysts are among the most active systems for the direct decomposition of NO_x, but suffer from rapid deactivation due to the saturation of the active metal centres by adsorbed oxygen. The generally accepted elementary reaction steps in the NO decomposition reaction on rhodium surfaces are shown in Eqs. (1)–(5), where “*” stands for a coordinatively unsaturated metal site.



According to Inderwildi et al. [5], the heat of adsorption of NO on rhodium(111) surfaces decreases with increasing oxygen coverage, but the adsorption of NO (Eq. (1)) remains thermodynamically favoured over the adsorption of O₂, which is endothermic at high oxygen coverage [6]. The dissociation of NO (Eq. (2)) takes place on rhodium surfaces at temperatures as low as 300 K and at low NO surface coverages [7], and therefore can be excluded as the rate determining step. The influence of different surface

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species on the selectivity of nitrogen desorption towards the formation of N_2 or N_2O (Eqs. (3) and (4)) is still under discussion [5]. TPD experiments by Aryafar and Zaera [8] showed two desorption peaks of N_2 from Rh(1 1 1) surfaces. The first maximum shifts from 700 to 560 K with increasing surface coverage, being in accordance with a second order kinetics. A second maximum at 460 K is only present when the coverage exceeds 0.2 monolayers. This peak does not shift with varying coverages, indicating a first order kinetics. These findings are consistent with earlier publications [9,10]. Significant desorption of O_2 (Eq. (5)) from Rh(1 1 1) surfaces occurs only at temperatures above 800–1100 K (depending on the surface coverage) [10,11], making the desorption of oxygen the rate determining step.

The lack of oxygen desorption at operating temperatures leads to catalyst deactivation by saturation of the surface with adsorbed oxygen. This inhibitory effect is intensified by the presence of excess oxygen in the feed gas. On the other hand, potential industrial and automotive applications require long term catalytic activity under oxidizing conditions. Therefore, current research aims at enhancing the oxygen desorption properties of rhodium catalysts.

In the present study, carbon nanotubes (CNT's) are used as a support material for rhodium catalysts. The impact of CNT's on the catalytic performance in the abatement of NO_x is investigated, focusing on their effect on oxygen desorption.

Among the different types of supports used in heterogeneous catalysis, carbon materials maintain an outstanding position due to their specific characteristics. Their resistance to acid and basic media, the possibility to control and modify their porosity and surface properties and the easy recovery of precious metals by support burning result in various catalytic applications. Several reviews on the use of carbon materials as catalysts or catalyst supports have been published [12–15].

Since the discovery of multi-wall carbon nanotubes (MWCNT's) by Iijima [16] in the early 1990s and the successive production of single-wall carbon nanotubes (SWCNT's) [17,18], the research on these new carbon forms has become one of the most active fields of nanoscience. Recently, CNT's produced in chemical vapor deposition (CVD) processes have become available in industrial scale, which has lead to an industrial interest, particularly in the area of fuel cell electrodes [19] and supported catalysts for fluid phase reactions [20]. The use of CNT's as a support material in heterogeneous catalysis has led to unconventional catalysts that have proved to be active in numerous reactions [21–24]. Yet, their application in the abatement of highly oxidizing substrates like NO_x seems paradoxal, in particular as NO_2 is known to be a favourable oxidizing agent for soot [25,26]. On the other hand, CNT's have been reported to possess superior oxidation resistance compared to other carbonaceous species [21].

Literature provides contradicting information about the impact of carbon on the performance of noble metal catalysts in De NO_x reactions. Different authors ascribe the outstanding catalytic activity of these systems to superior stabilization of M^0 by the carbon support, hydrogen storage or carbon acting as a reducing agent.

Wang et al. [27] investigated the reduction of NO over hydrogenated CNT's and 1 wt.% Pd on hydrogenated CNT's. They concluded that stored hydrogen as well as the CNT support serve as reducing agents for NO. To the best of our knowledge, the concept of CNT's acting as a reducing agent has not been transferred to Rh/CNT systems yet. Instead, NO decomposition on Rh/CNT's has been reported by Tang et al. [28], who stated that the CNT support is resistant against oxidation, and Luo et al. [29], who attributed the higher NO conversion over Rh/CNT's with respect to Rh/ γ - Al_2O_3 to the superior stabilization of Rh^0 on CNT's. Although both authors

observed the evolution of CO or CO_2 , oxidation of the support was not considered to play a major role for the catalytic performance.

In a recent publication on the catalytic abatement of NO using Rh/CNT catalysts, we pointed out the crucial role of CNT's as reducing agent to achieve the conversion of NO [30]. In this work, we present new results on the catalytic reduction of NO_x by Rh/CNT catalysts using NO and NO_2 as reactants and different pretreatments for CNT materials. For the first time, complete nitrogen and oxygen balances are shown to prove the stoichiometric consumption of the carbon support and provide further insight into the reaction mechanism. Structural changes of the catalyst during the time on stream are demonstrated by TEM micrographs.

2. Experimental

2.1. Catalyst preparation

For the preparation of Rh/CNT catalysts, MWCNT's (Baytubes C 150P, provided by Bayer Material Science) were agglomerated in distilled water, dried at 110 °C and sieved into a grain size of $300 \mu m < d_K < 500 \mu m$. Rh/CNT catalysts (3.25 wt.% Rh) were prepared by incipient wetness impregnation of CNT's with aqueous solutions of rhodium acetate ($Rh(CH_3COO)_2$), dried overnight at 110 °C in flowing argon and calcined for 8 h at 500 °C in flowing argon.

For the preparation of Rh/CNT(ox) catalysts, MWCNT's (Baytubes C 150P, provided by Bayer Material Science) were pretreated in boiling nitric acid for 2 h, washed several times with distilled water, dried at 110 °C and sieved into a grain size of $300 \mu m < d_K < 500 \mu m$. The as-made materials are denoted CNT(ox). Rh/CNT(ox) catalysts (3.25 wt.% Rh) were prepared by incipient wetness impregnation of CNT(ox) with aqueous solutions of rhodium acetate ($Rh(CH_3COO)_2$), dried overnight at 110 °C in air and calcined for 6 h at 250 °C in air.

Prior to the catalytic tests, all catalysts were heated to 300 °C at a ramp rate of 10 K/min in an argon flow of 100 ml/min and reduced for 1 h at 300 °C in flowing hydrogen at a flow rate of 100 ml/min.

2.2. Catalyst characterization

Dynamic single-point BET surface area analyses were performed on a Micromeritics Autochem 2910. Structural characterization of the freshly reduced and used catalysts was conducted by transmission electron microscopy (TEM) on a JEOL 100 CX. Rhodium particle size distributions were calculated from the measured sizes of 100 particles per sample.

2.3. Catalytic activity measurements

Initial and steady-state activities and selectivities in the catalytic abatement of NO and NO_2 in the temperature range of 250–450 °C were measured in the absence and presence of oxygen. Catalytic tests were performed in a fixed bed tube reactor with an inner diameter of 4 mm using 105 mg ($0.5 cm^3$) of catalyst. Feed gas mixtures contained 1000 ppm of the respective nitrogen oxide (NO or NO_2), helium as a balance and optional 5 vol.% of O_2 . The feed gas was run through the reactor at a flow rate of 100 ml/min and a gas hourly space velocity (GHSV) of $12,000 h^{-1}$. The effluent gas stream was analyzed on-line using fourier transform infrared spectroscopy (FTIR) and gas chromatography (GC). NO_2 , NO, N_2O , CO_2 and CO were analyzed by FTIR using a Perkin Elmer 1760 X spectrometer or a Biorad FTS 575 C spectrometer, each equipped with a LOT Oriel gas cell (path length 10 cm). N_2 , O_2 and CO_2 were analyzed by a micro gas chromatograph (Agilent 3000 A) equipped

with a molsieve coloumn (separation of N₂ and O₂), a plot Q coloumn (separation of CO₂) and a thermal conductivity detector.

3. Results and discussion

The interactions of Rh/CNT, Rh/CNT(ox) and CNT(ox) catalysts (the suffix “ox” stands for oxidative pretreatment of the support) with NO_x are evaluated using three distinct reaction conditions. Either NO or NO₂ is used as a reactant in the absence of oxygen in the feed gas. In addition, the catalytic activity of Rh/CNT(ox) towards NO in the presence of excess oxygen is evaluated. Throughout this work, the term NO_x is used for statements that apply to both NO and NO₂.

3.1. Abatement of NO_x in the absence of excess oxygen

In the absence of excess oxygen, Rh/CNT and Rh/CNT(ox) catalysts exhibit high initial and steady-state activities in the abatement of NO_x. Under the chosen reaction conditions, complete conversion of NO_x corresponds to a turnover frequency of $2.17 \times 10^{-3} \text{ s}^{-1}$ based on the total amount of rhodium present in the catalysts. Complete conversion of NO and NO₂ with 100% N₂ selectivity is attained at reaction temperatures of 450 °C over Rh/CNT and 400 °C over Rh/CNT(ox). In contrast to this, pure CNT(ox) reduces NO₂ to NO, but further conversion of NO is negligible in the studied temperature range. An overview over the steady-state conversions and product distributions is given in Table 1.

The lack of conversion of NO over the pure CNT(ox) material implies that NO is exclusively decomposed on the active metal centres of the rhodium catalysts. The resulting nitrogen species recombine and desorb in the form of N₂. The formed oxygen species react with the carbon support. CO and CO₂ are formed and desorbed from the catalyst surface. Stoichiometric amounts of carbon oxides in respect of the amount of oxygen provided by the dissociation of NO_x are detected in the effluent gas stream. No desorption of molecular oxygen is observed. The net reaction is therefore considered as a rhodium-mediated reduction of NO_x with carbon as the reducing agent.

A detailed view of the reaction monitoring using Rh/CNT and Rh/CNT(ox) catalysts is shown in Figs. 1 and 2 for the abatement of NO and NO₂, respectively. Complete nitrogen and oxygen balances are given.

Table 1

NO_x conversion and product distribution of the catalytic abatement of NO and NO₂ using Rh/CNT, Rh/CNT(ox) and CNT(ox) catalysts under steady-state conditions.

	T (°C)	Abatement of NO			Abatement of NO ₂			
		x (NO)	y (N ₂ O)	y (N ₂)	x (NO ₂)	y (NO)	y (N ₂ O)	y (N ₂)
Rh/CNT	250	2	1	5	30	26	1	0
	300	3	1	6	78	70	1	0
	350	9	0	15	98	84	0	3
	400	52	0	52	100	67	0	22
	450	99	0	97	100	0	0	83
Rh/CNT(ox)	250	3	1	2	55	54	0	3
	300	7	0	5	97	92	0	2
	350	36	0	31	100	78	0	20
	400	99	0	94	100	0	0	93
	450	98	0	96	100	2	0	92
CNT(ox)	250	0	0	0	39	39	0	0
	300	0	0	0	80	76	0	0
	350	3	0	0	99	92	0	3
	400	3	0	2	100	91	0	3
	450	5	0	1	100	91	0	3

Conditions: 105 mg of catalyst, 1000 ppm NO in He or 1000 ppm NO₂ + 250 ppm O₂ in He, GHSV = 12,000 h⁻¹ (x = conversion (%); y = yield (%); all data given in N₂ equivalents).

It can be seen in Fig. 1 that in the initial phase of the NO abatement experiments at 250 °C NO is depleted and N₂ as well as small amounts of N₂O and CO₂ evolve. This is ascribed to the reduction of NO by hydrogen that has been stored in the catalyst during the reductive pretreatment (indicated by the temporary detection of trace amounts of water in the effluent gas stream) and by labile surface oxygen compounds (SOC) [31] and defect sites on the CNT's. The effect is more pronounced for the Rh/CNT(ox) catalyst, which is due to the increased number of SOC and defect sites implemented by the oxidative pretreatment of the support [32]. Similar effects occur after increasing the temperature to 300 °C. Using Rh/CNT(ox), over-stoichiometric amounts of N₂ and CO₂ are detected upon the increase in temperature to 350 °C, which is due to the reduction of NO that has been stored in the catalyst at lower reaction temperatures and the total oxidation of remaining SOC and/or defect sites by adsorbed oxygen originating from the dissociation of stored NO. For 30 min, complete conversion of NO is achieved. After 30 min, the conversion drops to 36%. Using Rh/CNT, a similar but far less pronounced effect is seen at 400 °C. This indicates that SOC and defect sites significantly increase the reactivity of the catalyst. Quantitative conversion of NO is achieved at 400 and 450 °C for Rh/CNT(ox) and at 450 °C for Rh/CNT for the duration of the experiment. Thus, the oxidatively pretreated system is more effective for NO reduction at low temperatures.

For both catalysts, the reaction products are N₂ and oxides of carbon which are formed by the reaction of adsorbed oxygen from NO dissociation with the CNT supports. No desorption of molecular oxygen is observed. Using the Rh/CNT catalyst, apart from minor initial effects CO_x are always generated in stoichiometric amounts with respect to the amount of adsorbed oxygen produced by the dissociation of NO (within the error of measurement). Using Rh/CNT(ox), the concentration of CO_x slightly exceeds the reaction stoichiometry due to the significant number of functional groups providing additional oxygen for CO_x formation.

The ratio of CO/CO₂ ratio also differs with the catalyst used. While both catalysts predominantly produce CO₂ at temperatures up to 400 °C, Rh/CNT generates a higher fraction of CO than Rh/CNT(ox) at 450 °C (see Table 2).

The weight loss of the catalysts during the reaction is 4 and 11 mg for Rh/CNT and Rh/CNT(ox), respectively. As 1 h of full conversion of NO to N₂ and CO₂ corresponds to 1.6 mg of carbon loss, these results are in good agreement with the stoichiometric consumption of carbon from Rh/CNT and the slightly over-stoichiometric consumption from Rh/CNT(ox) (taking into account the higher activity of Rh/CNT(ox)). These results also make clear that the catalysts can withstand a significant but limited time on stream.

The abatement of NO₂ requires the reduction of NO₂ to NO prior to the already discussed reaction pathways [33–35]. The results presented in Table 1 suggest that this reaction step can take place on the pure carbon support but is accelerated by the presence of active metal centres (compare the conversion of NO₂ over CNT(ox) and Rh/CNT(ox)). This reduction leads to adsorbed oxygen on the catalyst surface, which is subsequently desorbed in the form of CO and CO₂. For Rh/CNT(ox), the reduction of NO₂ is incomplete at 250 °C and quantitative from 300 °C on. For CNT(ox) and Rh/CNT, complete reduction of NO₂ is achieved at 350 °C or higher. These conversions are significantly higher than the equilibrium conversions of the thermal decomposition of NO₂ into NO and O₂ in this temperature range ($x_{\text{equilibrium}}(\text{NO}_2) = 66\%$ at 300 °C and 83% at 350 °C in the reactant gas mixture as calculated using the commercial HSC Chemistry[®] 5.1 program [36]). The reaction monitoring for the abatement of NO₂ using Rh/CNT and Rh/CNT(ox) catalysts is shown in Fig. 2.

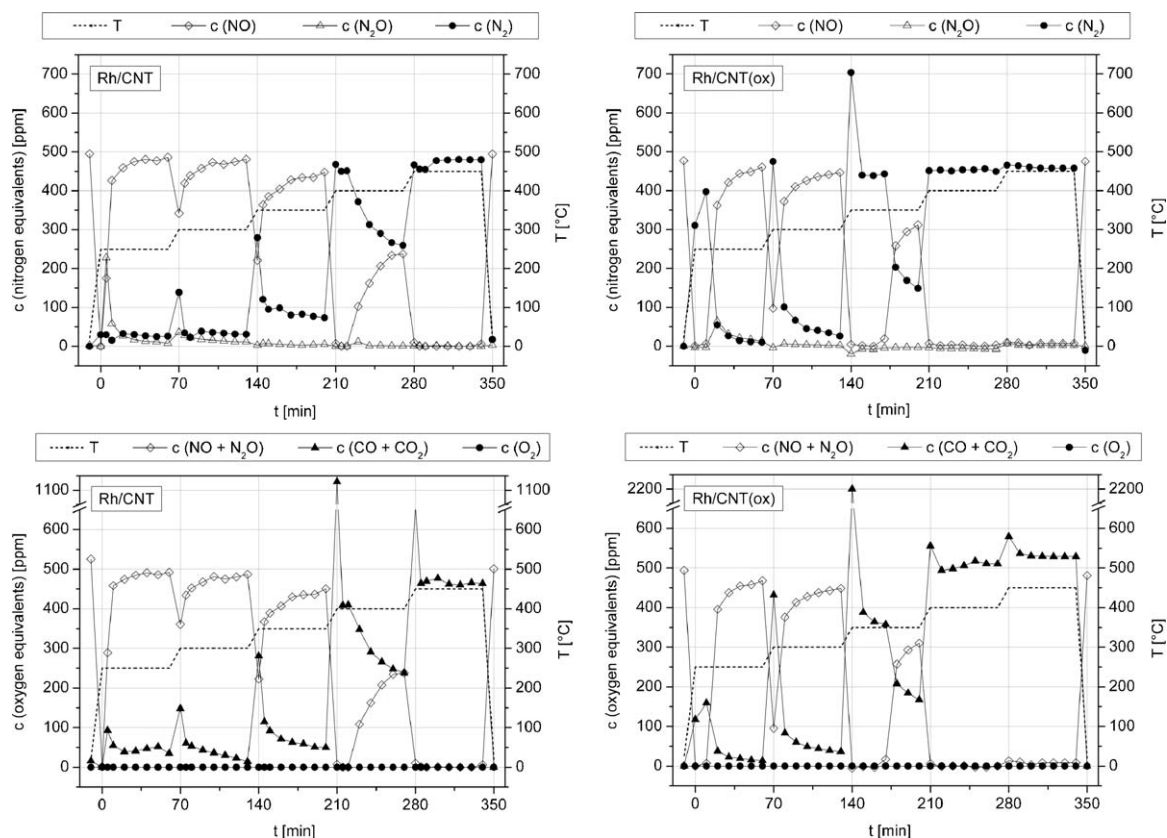


Fig. 1. Reduction of NO over Rh/CNT and Rh/CNT(ox) in the absence of excess oxygen. Conditions: 105 mg of catalyst, 1000 ppm NO in He, GHSV = 12,000 h⁻¹. Concentrations of reactant and product gases are normalized to equivalents of N₂ or O₂ and plotted as a function of reaction temperature and time on stream. The first and last data points are bypass measurements showing the composition of the feed gas.

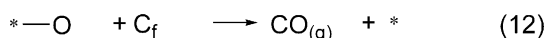
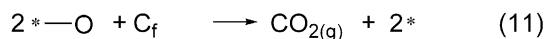
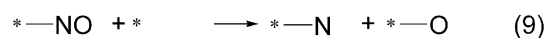
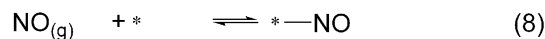
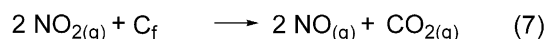
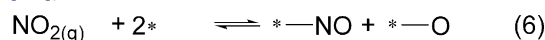
Once NO₂ is reduced to NO, the experiments proceed analogue to the NO abatement reactions discussed above. This observation is valid for initial and steady-state reactions as well as for storage effects (compare Fig. 2 with Fig. 1). At 350 °C, the initial full conversion over Rh/CNT(ox) drops already after 10–20 min (as opposed to 30 min in the NO abatement reaction). This is due to the fact that the dissociation of a molecule of NO₂ results in twice as much adsorbed oxygen than the dissociation of a molecule of NO. Accordingly, SOC and defect sites are burned more quickly. The same tendency is observed for the analogue effect at 400 °C using Rh/CNT. In this context, it is to be noted that the stoichiometric oxidation of carbon during the abatement of NO₂ must lead to twice as much carbon oxides than during the abatement of NO, which is confirmed by our experimental data. As in the NO abatement experiments, no significant desorption of molecular oxygen from the catalysts is observed. Instead, the amount of approx. 250 ppm of O₂ present in the NO₂ feedgas mixture for technical reasons (provided as is by the gas supplier) is partly consumed, depending on the reaction temperature. Therefore, the amount of CO₂ released by the catalysts is higher by the amount of O₂ from the feed that is oxidized than expected for the stoichiometric reduction of NO_x. Taking this into account, the release of CO_x is again stoichiometric using Rh/CNT and slightly over-stoichiometric using Rh/CNT(ox) in the steady-state. Initial effects are found to be more pronounced than in the abatement of NO because of the higher oxidation strength of NO₂.

Analogue to the abatement of NO, the CO/CO₂ ratio slightly differs with the catalyst used. While both catalysts predominantly produce CO₂ at temperatures up to 400 °C, Rh/CNT generates a higher fraction of CO than Rh/CNT(ox) at 450 °C (see Table 2).

The weight loss of the catalysts during the reaction is 9 and 20 mg for Rh/CNT and Rh/CNT(ox), respectively. One hour of full

conversion of NO₂ to N₂ and CO₂ corresponds to 3.2 mg of carbon loss. Taken into account the higher activity of Rh/CNT(ox), these results are in good agreement with the stoichiometric consumption of carbon using Rh/CNT and the slightly over-stoichiometric consumption using Rh/CNT(ox).

The results shown so far indicate that the NO_x abatement reactions using rhodium catalysts supported on CNT's proceed via the following main reaction steps ("*" stands for a coordinatively unsaturated rhodium surface site, C_f stands for a free carbon site [31]):



Eqs. (6) and (7) are only applicable to the abatement of NO₂. The abatement of NO₂ on rhodium surfaces exclusively taking place via NO is in good agreement with literature [33–35]. According to our results, the reduction of NO₂ to NO can occur on the active metal centres as well as on the carbon support. Eqs. (8) and (9) show the adsorption and dissociation of NO on the active metal centres. Dissociation of NO on the carbon support can be excluded because

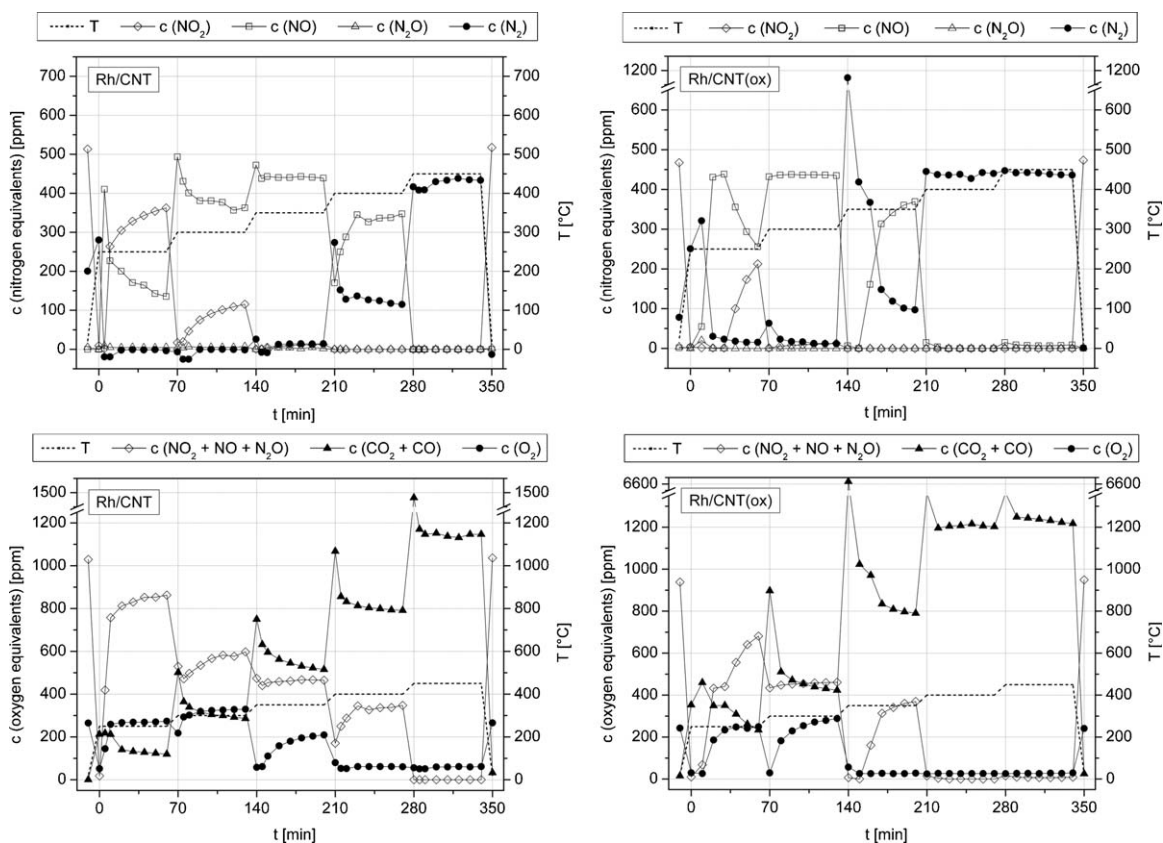
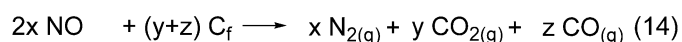


Fig. 2. Reduction of NO_2 over Rh/CNT and Rh/CNT(ox) in the absence of excess oxygen. Conditions: 105 mg of catalyst, 1000 ppm NO_2 and 250 ppm O_2 in He, GHSV = 12,000 h^{-1} . Concentrations of reactant and product gases are normalized to equivalents of N_2 or O_2 and plotted as a function of reaction temperature and time on stream. The first and last data points are bypass measurements showing the composition of the feed gas.

of the absence of catalytic activity of the pure CNT's. Eqs. (10)–(12) show the desorption pathways for nitrogen and oxygen in the form of N_2 , CO and CO_2 . According to the oxygen balances presented in Figs. 1 and 2, oxygen desorption proceeds exclusively via the stoichiometric oxidation of the support material and the formation of CO and CO_2 . The consequential net reactions are shown in Eqs. (13) and (14):



$$\text{with } x = (y + 0.5z)$$

With regard to the stoichiometries of the overall processes, the abatement of NO_x using Rh/CNT and Rh/CNT(ox) catalysts must be

considered as a stoichiometric reduction of NO_x with carbon as the reducing agent, catalyzed by rhodium particles.

Further endorsement of the support material acting as reducing agent is provided by TEM micrographs of the Rh/CNT(ox) catalysts before and after the catalytic test runs. The structural changes of the catalysts during the NO abatement procedure are illustrated in Fig. 3a (fresh Rh/CNT(ox) after reductive pretreatment) and Fig. 3b (used Rh/CNT(ox)).

The rhodium particles of the fresh catalyst have an average diameter (d_m) of 2.5 nm, exhibit a narrow size distribution and are evenly dispersed on the CNT surface, with some agglomeration at nanotube entanglements. The CNT structures are intact.

After a time on stream of 340 min, the morphology of the catalyst support is partly destroyed. Remaining nanotube structures show an increased amount of defects. A considerable accumulation of the rhodium particles on the remaining nanos-

Table 2

NO_x conversion and CO/CO_2 release of the catalytic abatement of NO and NO_2 using Rh/CNT and Rh/CNT(ox) catalysts under steady-state conditions.

Catalyst	T (°C)	Abatement of NO				Abatement of NO_2			
		x (NO_x)	y (CO_2)	y (CO)	y (O_2)	x (NO_x)	y (CO_2)	y (CO)	y (O_2)
Rh/CNT	250	2	1	0	0	16	12	0	1
	300	3	3	0	0	42	28	0	6
	350	9	11	0	0	55	50	0	–5
	400	52	50	0	0	66	77	0	–20
	450	99	54	43	0	100	85	27	–20
Rh/CNT(ox)	250	3	3	0	0	28	25	0	1
	300	7	8	0	0	51	45	0	5
	350	36	35	0	0	61	83	0	–23
	400	99	97	9	0	100	122	5	–23
	450	98	78	32	0	99	107	21	–22

Conditions: 105 mg of catalyst, 1000 ppm NO in He or 1000 ppm NO_2 + 250 ppm O_2 in He, GHSV = 12,000 h^{-1} (x = conversion (%); y = yield (%); all data given in O_2 equivalents).

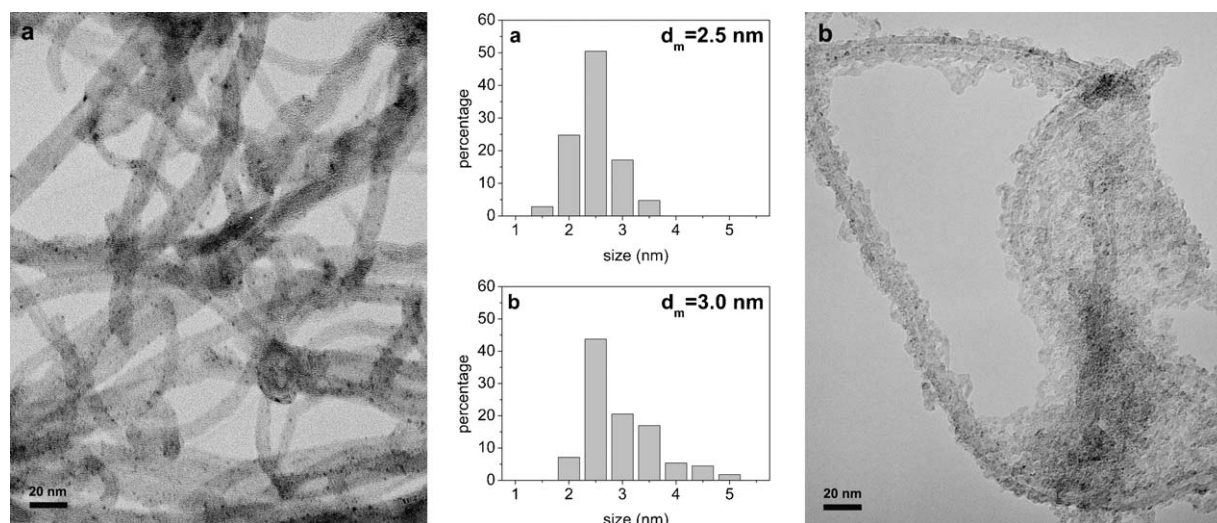


Fig. 3. (a) Transmission electron micrograph and Rh particle size distribution of fresh Rh/CNT(ox) catalyst after reduction at 300 °C in H₂. (b) Transmission electron micrograph and Rh particle size distribution of used Rh/CNT(ox) catalyst after a catalytic test run with 1000 ppm of NO in the absence of excess oxygen (time on stream = 340 min).

structured parts of the support is observed. The particles show an increased d_m value of 3.0 nm and a broadened size distribution.

BET surface measurements of a CNT based material at different stages of catalyst preparation and catalytic test procedures support the finding that the carbon support interacts with oxidants during the preparation procedures as well as during catalysis (Table 3).

The initial surface area of the as-received CNT's is increased during oxidative treatment in nitric acid due to the development of defect sites. The number of defects and accordingly the surface area is further increased during the calcination process in air. The support acting as the reducing agent in the catalytic test run has the same effect, which corresponds well with the increase of defect sites observed by TEM.

3.2. Abatement of NO in the presence of excess oxygen

The presence of excess oxygen in the feed gas leads to a rapid oxidation of the CNT support and formation of CO and CO₂, resulting in the degradation of the catalysts and a complete loss of catalytic performance (results not shown).

Apart from a slight initial activity at 250 °C, the conversion of NO to N₂ is only observed in the first 30 min at 350 °C using the Rh/CNT(ox) catalyst. The conversion is quantitative during this period, but breaks down to zero afterwards. At 400 and 450 °C, no N₂ is produced. The loss of activity is due to the catalyst support being almost completely burned within the first 30 min at 350 °C. During this time, the 5 vol.% oxygen in the feed gas are completely consumed and the CO₂ release is orders of magnitude higher than expected for the stoichiometric reduction of NO. The weight loss of the catalyst during the time on stream is 100 mg, which equals 98 wt.% of the support material.

The coexistence of 1000 ppm NO and 5 vol.% O₂ in the gas feed has no significant effect on the burn-off temperature of Rh/CNT(ox)

with respect to the presence of oxygen alone. This is shown by exposing Rh/CNT(ox) to 5 vol.% O₂ in He without the addition of NO. The burn-off temperature in this case is also found to be 350 °C.

A reference measurement using pure CNT(ox) revealed that the rapid oxidation of the CNT's by bulk oxygen at 350 °C is catalyzed by the rhodium particles on Rh/CNT(ox). The onset temperature for the rapid thermal oxidation of CNT(ox) is 450 °C.

4. Conclusions

The outstanding catalytic activity of Rh/CNT and Rh/CNT(ox) catalysts in the abatement of NO and NO₂ in the absence of excess oxygen without the use of additional reducing agents is attributed to the support material itself acting as the reducing agent. The formation and desorption of CO_x effectively prevents the saturation of the active centres with adsorbed oxygen species that would otherwise lead to deactivation as observed for other rhodium catalysts. No desorption of molecular oxygen was observed. Controversially, other authors ascribe the performance of Rh/CNT catalysts to strong metal-support interactions.

The steady-state reaction observed in the absence of excess oxygen is a catalytic reduction of NO_x with carbon as the reducing agent, despite its mechanistic similarity to direct NO_x decomposition concerning the NO dissociation step. Whereas in classic SCR processes the reducing agent is needed to form a reaction intermediate with NO to facilitate the dissociation of the N–O bond, the N–O bond scission step proceeds independent of any reducing agent on Rh/CNT catalysts. Yet the net reaction includes a stoichiometric consumption of a reducing agent and therefore must be considered as a catalytic reduction of NO_x. This finding is in contrast to previously published results describing Rh/CNT catalysts as active systems in the direct NO decomposition reaction without regard to the crucial role of the stoichiometric oxidation of the carbon support.

An oxidative pretreatment of the support material enhances the catalytic activity of rhodium catalysts supported on CNT's. The temperature required for the quantitative conversion of NO_x to N₂ is 50 °C lower for the Rh/CNT(ox) catalyst than for the Rh/CNT catalyst.

Rh/CNT and Rh/CNT(ox) catalysts exhibit high steady-state activities in the abatement of NO_x for a limited time. The lifetime of the catalysts is determined by the stoichiometric consumption of the support material. While the catalysts withstand a considerable

Table 3

Development of the BET surface area of a CNT based material during catalyst preparation and during a catalytic test run with 1000 ppm of NO in the absence of excess oxygen (time on stream = 340 min).

Material	BET (m ² /g)
CNT (as-received)	271
CNT(ox)	291
Rh/CNT(ox) (fresh, reduced)	299
Rh/CNT(ox) (used)	321

yet limited time on stream in the absence of oxygen, they are not at all suitable for DeNO_x catalysis in the presence of excess oxygen.

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